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Method for regulating the fuel concentration in a fuel mixture of a fuel cell which contains alcohol or ether as fuel and water, and fuel cell system

Description

The invention relates to a method for regulating the fuel concentration in a fuel mixture for a fuel cell which is formed by an alcohol or an ether as fuel and water, and to a fuel cell system, containing at least one fuel cell, which can be operated with a fuel mixture consisting of an alcohol or an ether as fuel and water, and at least one mixing space, which is connected to in each case one controllable fuel inlet, and at least one fuel-mixture feedline, which connects the at least one mixing space to in each case the at least one fuel cell.

At the date of this application, fuel cell systems of the abovementioned type have already been known for over 30 years (cf. for example *W. Vielstich; "Brennstoffelemente" [Fuel Elements] Verlag Chemie, Weinheim 1965, pages 73-93* and *L. Oniciu; "Fuel Cells", Abacus-Press, Kent, 1976, pages 93-98)*. The alcohol, for example methanol, as fuel, mixed with water to form a fuel mixture, is fed to a fuel cell, where it is directly converted into electrical energy. Alcohol contents of between 1% by volume and 5% by volume in the fuel mixture have proven particularly advantageous for operation of a fuel cell of this type. One problem with the operation of fuel cells of this type is that of keeping the alcohol concentration of the fuel mixture as constant as possible. This applies equally to fuel cells which use alcohol and fuel cells which use ether as the fuel.

DE 197 01 560 A1 has disclosed a fuel cell system in which a liquid fuel mixture comprising a fuel and a coolant is fed to the anode space of a fuel cell. DE 196 28 888 C1 discloses a fuel cell which can be operated, inter alia, with a fuel mixture of fuel and

water. In this case, the efficiency of the fuel cell is increased by an alternating operating pressure. DE 44 25 634 C1 has disclosed a method and a device for the metered supply of methanol and/or water from a reservoir, via a conveyor pipe, to a fuel cell system. In this case, a delivery pump is used to convey a constant mass flow rate from the reservoir into the conveyor line, and the differential pressure between conveyor line and fuel cell system is set to a predetermined value with the aid of a differential pressure regulator, so that the quantity of methanol and/or water supplied can be set, for example, by varying the opening and closing times of a solenoid valve. The abovementioned prior art fails to disclose either a method or a device for regulating the fuel concentration in the fuel mixture.

DE 35 08 153 has disclosed the regulation of the concentration of the fuel within a fuel mixture using a fuel cell which is operating in idling mode. This document exploits the fact that the idling potential of a fuel cell is dependent on the fuel concentration. However, this type of regulation is highly complex and therefore very expensive.

It is now an object of the present invention to provide a method of the type described in the introduction which is simpler than the prior art and at the same time is effective, and to provide a fuel cell system which is suitable for carrying out this method.

With regard to a method for regulating the fuel concentration in a fuel mixture of a fuel cell which contains an alcohol or ether and water, this object is achieved by the fact that the fuel is fed via a controllable fuel inlet to a mixing space, from where the fuel mixture is fed, via a fuel-mixture feedline, to the fuel cell via a membrane which is arranged downstream of the fuel inlet, as seen in the direction of flow, delimits a measurement chamber and is selectively permeable to water and the fuel, a liquid or gaseous measurement mixture with a fuel

concentration of less than 1% by volume or more than 5% by volume, depending on the quantity of fuel which permeates into the measurement chamber from the fuel mixture per unit time, being produced in the measurement chamber, whereupon the fuel concentration in the measurement mixture is determined and the fuel inlet is controlled as a function of the fuel concentration in the measurement mixture.

Therefore, the regulation is achieved by the fact that it is not directly the fuel concentration in the fuel mixture which is determined, but rather the fuel concentration in a measurement mixture in which the fuel concentration is within a range which can be measured with sufficient accuracy and speed using known sensors. The fuel concentration in the measurement mixture is directly dependent on the fuel concentration in the fuel mixture, so that it can be controlled by measuring the fuel content in the measurement mixture.

The method according to the invention can be carried out in such a way that, to produce the measurement mixture in the measurement chamber, a carrier liquid or a carrier gas is used to dilute and/or remove the permeated fuel. The permeated fuel can also be consumed at electrodes in the measurement chamber, so that it is not imperative that the fuel be removed by the carrier liquid or the carrier gas. The specified fuel concentrations can also be achieved even without a carrier liquid or a carrier gas, by means of suitable membranes: for example, the membrane may be more permeable to the fuel than to water by more than one order of magnitude, so that a measurement mixture with a fuel concentration of less than 1% by volume even down to the ppm range can be formed in the measurement chamber from the permeated fuel and the permeated water. Conversely, if the permeability of the membrane is higher for water than for the fuel, it is possible to form measurement mixtures in which the fuel concentration is over 5, preferably over 10% by volume. Membranes which are suitable for this purpose are known

(cf. for example *H. Strahtmann; "Membranes and Membrane Separation processes", B. Elvers, S. Hawkins, G. Schulz (Ed.); "Ullmanns Encyclopedia of Industrial Chemistry", Vol. A. 16. VCH, Weinheim, 1990, pages 187-263*).

The method according to the invention may also be implemented in such a way that the fuel concentration of the measurement mixture, in the case of values above 10 or 5% by volume, is determined by means of a liquid sensor.

The method according to the invention may also be carried out in such a way that the fuel concentration of the measurement mixture is determined by means of density or viscosity measurements.

The method according to the invention may also be carried out in such a way that the fuel concentration of the measurement mixture is determined by means of optical methods, for example by means of infrared absorption. Optical sensors which are suitable for this purpose, in particular for assessing the CH vibrations of the fuel, are also known (cf. for example *A. Brittain et al. (Ed.) "Optically Based Methods for Process Analysis", S. PIE Proceedings Vol. 1681, Somerset, NJ, USA, 1992*).

The method according to the invention may also be carried out in such a way that the fuel concentration of the measurement mixture, in the case of values below 1.0 or 0.1% by volume, is determined by means of a gas sensor. A gas sensor of this type has a semiconductor element which changes its electrical properties as a function of the concentration of the fuel. A gas sensor of this type and its use in a measurement chamber delimited by a silicone membrane is likewise known in connection with bioreactors (cf. *FMC-Handbuch der Biotechnologie [FMC Biotechnology Manual] Kempe GmbH, Berlin*). Furthermore, it is in this case possible to carry out the determination by recording the conductivity and by infrared absorption.

In a fuel cell system of the type described in the introduction, the abovementioned object is achieved by the fact that the fuel cell system has at least one measurement probe, which is arranged downstream of the fuel inlet, as seen in the direction of flow of the fuel mixture, and comprises

a) a measurement chamber,

b) a membrane which delimits the measurement chamber, is in contact with the fuel mixture, is selectively permeable to the fuel and/or water and is used to produce a liquid or gaseous measurement mixture with a fuel concentration of less than 1% by volume or more than 5% by volume depending on the quantity of fuel which has permeated into the measurement chamber from the fuel mixture per unit time, and

c) a sensor for determining the fuel concentration in the measurement mixture,

and that the fuel cell system has means for controlling the fuel inlet as a function of the fuel concentration in the measurement mixture.

The invention furthermore provides for the sensor to be a gas, liquid, infrared absorption, density measurement, optical or conductivity measurement sensor.

In the text which follows, an embodiment or a configuration is described, by way of example, for the methods according to the invention and the fuel cell systems according to the invention in connection with methanol combustion. In the drawing:

Fig. 1 diagrammatically depicts the structure of a fuel cell system which uses methanol as fuel, and

Fig. 2 diagrammatically depicts an enlarged excerpt from the arrangement shown in Fig. 1, with a measurement probe coupled to a fuel-mixture feedline.

The fuel cell system shown in Fig. 1, which uses methanol as fuel, comprises a fuel cell 1 with a fuel chamber 2 and a reactant chamber 3. The fuel mixture, which consists of methanol and water, is fed to the fuel chamber 2 via the fuel-mixture feedline 4, the methanol concentration in the fuel mixture amounting to approximately 4% by volume. The reactant chamber 3 is supplied with air via a reactant feedline. The exhaust gas, which is a water/air mixture, is discharged from the reactant chamber 3 via the exhaust-gas line 6.

The fuel mixture, in which the methanol level has been reduced by the amount consumed, is discharged from the fuel chamber 2 via the residual fuel discharge line 7 and is passed to an intermediate store 8. A recycling pump 9 is connected to the intermediate store 8, via which pump the fuel mixture of reduced methanol content is pumped into the fuel-mixture feedline 4 and therefore to the fuel chamber 2. The fuel mixture is therefore circulated.

To enable the fuel mixture which enters the fuel chamber 2 to have the requisite methanol concentration, methanol is pumped out of a methanol store 10, via a methanol pump 11, into a mixing space 12, where it is mixed with the fuel mixture of reduced methanol content from the intermediate store 8. The mixing space 12 is symbolically represented in enlarged form in Fig. 1 but may actually also simply be a part of the fuel-mixture feedline 4. The pumping capacity of the methanol pump 11 is controllable.

To be able to ensure that the methanol content of the fuel mixture which enters the fuel chamber 3 is as constant as possible, the methanol concentration is regulated. To do this, a parameter which is directly dependent on the methanol concentration in the fuel mixture is measured. The area surrounded by a dashed circle in Fig. 1 is shown on an enlarged scale in Fig. 2. Fig. 2 shows a measurement probe 13 which is fitted to the fuel-mixture feedline 4. The measurement probe

13 has a membrane 14 which is in direct contact with the fuel mixture flowing past. The membrane 14 is selectively permeable to water and methanol, in such a manner that a measurement mixture which consists of water and methanol and has a methanol content in the ppm range is formed in the measurement chamber 16 which is delimited by the walls 15 of the measurement probe 13 and of the membrane 14. In the measurement chamber 16 there is a methanol sensor 17 which is highly effective in this concentration range. The measured variable which is generated by the methanol sensor 17 as a function of the methanol concentration in the measurement mixture is transmitted via the measurement line 18 to a control unit 19 (Fig. 1) which therefore controls the methanol pump 11 as a function of the methanol concentration in the measurement mixture. Since the methanol concentration in the measurement mixture is directly dependent on the methanol concentration in the fuel mixture in the fuel feedline 4 at the location of the measurement probe 13, this control arrangement can be used to maintain a substantially constant methanol concentration in the fuel mixture.

List of reference numerals

1	Fuel cell
2	Fuel chamber
3	Reactant chamber
4	Fuel-mixture feedline
5	Reactant feedline
6	Exhaust-gas line
7	Residual fuel discharge line
8	Intermediate store
9	Recycling pump
10	Methanol store
11	Methanol pump
12	Mixing space
13	Measurement probe
14	Membrane
15	Wall
16	Measurement chamber
17	Methanol sensor
18	Measurement line
19	Control unit